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Synthesis and Characterization of Hollow Silica Spheres

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Abstract

The synthesis and characterization of mono-dispersed silica hollow spheres using polystyrene (PS) spheres as template from the hydrolysis and condensation of tetraethylorthosilicate (TEOS) is presented. Successive washing steps with toluene and subsequent calcination at different temperatures were performed, in order to remove the PS template. Furthermore, the PS core removal was studied using different calcination temperatures, but without the prior washing with toluene. The morphology of the materials was studied by scanning electron microscopy and by transmission electron microscopy. A shell formed by silica nanoparticles with 50 nm diameter, being the layer of 100 nm thickness, was observed when using a low concentration of catalyst in the sol-gel reaction. The textural properties of the silica coating, obtained from N_2 adsorption-desorption isotherms, depend on the catalyst amount added for the TEOS hydrolysis. From the Fourier transform infrared spectra and the results of the thermogravimetric analyses, it was found that the almost complete removal of the polystyrene core can be directly achieved by calcining at 500 °C, without the need of carrying out any washing and minimizing the formation of cracks in the silica hollow spheres.

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Keywords: silica, hollow spheres, template, polystyrene, TEOS

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1. Introduction

In the recent years considerable interest has been generated on the synthesis of hollow spherical materials which currently are significant in science and technology, due to the various possible applications because of their unique properties.

Among these materials, the hollow silica spheres which have excellent mechanical properties and high thermal stability can be mentioned. The hollow spheres are now used in the preparation of materials specially designed for catalysis and medicine, as supports of catalytically active compounds and in the controlled release of compounds with biological activity used in pharmaceutical drugs (Huang et al., 1999); the hollow interior of these spheres makes possible the encapsulation of a wide variety of molecules.

The properties of these materials are interesting from a scientific point of view because they have nice characteristics such as low density, high surface area, high permeability and good biocompatibility.

A variety of templates and preparation methods have been used for the synthesis of hollow silica spheres. The Stöber´s method emerges as the most efficient to obtain a silica coating with uniform morphology, through a simple control of the hydrolysis and condensation of tetraethylorthosilicate (TEOS) in an ethanol-water solution using ammonium hydroxide as catalyst for the hydrolysis of TEOS (Stöber et al., 1968).

Soft templates can be used, such as surfactants at oil-water or air-water interfaces, forming droplets around which silica is deposited. These soft templates often show a low stability and lead to spheres with polydisperse sizes. To overcome these problems, hard templating methods have been used to fabricate mesoporous silica hollow spheres by using polymers (Theng et al., 2013), being the polystyrene (PS) the most used.

Caruso et al. (1998, 2001) have obtained hollow spheres using a polymer as a core and the shell prepared layer by layer (LbL). The basis of the LbL technique is the electrostatic attraction between the charged species deposited. Also, Shiho and Kawahashi (2000) reported the preparation of metal oxides hollow spheres using polystyrene as a template and polyvinyl pyrrolidone (PVP).

In the literature (Lu et al., 2004), it is informed that the PS core is removed from the spheres by successive washings with organic solvents including toluene, tetrahydrofuran (THF) or THF/acetone mixtures, followed by a heat treatment of the materials. Principal disadvantages of this procedure were the synthesis time, the relative high cost and the poor eco-compatibility with the environment.

As alternative to this procedure, high calcination temperatures were used, in order to eliminate the template and so obtain hollow spheres, being this procedure the most recommended due to the absence of organic waste, the relative low cost and the short completion time.

In the present work, the influence of different operative variables employed in the synthesis of mono-dispersed silica hollow spheres using polystyrene spheres as template is studied. Specifically, the effect of diverse polymerization initiators to obtain the template, different amounts of catalyst for the tetraethylorthosilicate hydrolysis in the sol-gel reaction to obtain the silica coating, different methods to eliminate the polystyrene core and various calcination temperatures is presented. The aim is to observe the influence on the final characteristics of the materials designed to be used as support of a catalytically active compound.

2. Experimental procedures

2.1. Synthesis of polystyrene template

Monodisperse polystyrene spheres were synthesized by the polymerization of styrene (Aldrich, > 99%) in the presence of PVP (Aldrich, PM = 29000) as a surfactant agent or dispersion stabilizer (Hong et al., 2010).

4.4 ' azobis 4-cyanovaleric acid (Aldrich, > 98%) or potassium persulphate (KPS) (Mallinckrodt, > 99%) were used as polymerization initiators in a concentration of 10% w/w respect to the styrene.

A mixture of 10 g of styrene and PVP, in a PVP to styrene ratio of 3% (w/w), was dissolved in 30 ml of ethanol or ethanol-water mixture depending the initiator to be used, and then was poured into a 250 cm^3 reactor, fitted with a reflux condenser, a temperature controller and a magnetic stirrer.

N_2 was bubbled for 15 min in order to remove oxygen from the reactor. When the system temperature was increased up to 70 ºC, the initiator (ACVA or KPS) dissolved in ethanol or ethanol-water respectively was added, and the polymerization was carried out at 300 rpm for 24 h.

After this time, the latex was washed several times with ethanol and stored in the form of suspension in the solvent.

2.2. Coating the polystyrene spheres with silica

A suspension of polystyrene spheres in absolute ethanol was submitted to ultrasound during 10 min to obtain an homogeneous suspension.

A modification of the Stöber method was used for the synthesis of silica. The original method develops via hydrolysis/condensation of TEOS in a mixture of water/alcohol/ammonium hydroxide solution (Stöber et al., 1968). To obtain the coating, in the present work ethanol was employed as a solvent, TEOS as a precursor of silica, and ammonium hydroxide (28% w/w) as a catalyst. NH_4OH was added in different amounts (1 and 7 ml) with the purpose of studying the effect of the concentration in the sol-gel reaction. It may be noted that the coating with silica was carried out using polystyrene microspheres prepared with ACVA as the polymerization initiator due to the better characteristics obtained with this compound.

The condensation reaction was performed at 50 °C with continuous stirring for 24 h. After this period of time, the coated spheres were separated by centrifugation and washed three times with distilled water to remove surfactant residues. Then they were dried at room temperature for 24 h and finally in an oven at 60 º C.

2.3. Obtaining the hollow silica spheres

For the synthesis of the hollow silica spheres from the materials obtained using 1ml of NH_4OH as catalyst in the sol-gel reaction, the elimination of the polystyrene core was carried out by successive extractions with toluene and subsequent calcination at different temperatures. Also the elimination of the template was studied through heat treatment without previous extraction, in order to compare both methodologies.

To remove the template, a weighed amount of coated spheres were placed in a beaker with a known volume of toluene and left under stirring at room temperature for 5 h. After this time, the spheres were separated from the supernatant liquid by centrifugation and a new extraction was carried out by repeating the methodology previously described. When this procedure was completed, the solid was separated from the supernatant liquid and it was dried at room temperature. Then, the extracted spheres were separated into four portions and calcined at 200, 300, 400 and 500 °C.

In parallel, coated spheres were calcined at different temperatures (200, 300, 400 and 500 °C) without prior extraction with toluene. The temperature was increased 50 ºC at 1 h time intervals for each case, being the heating rate 1 °C/min.

The solids were identified with the following nomenclature according to the applied treatment (Table 1).

Table 1. Sample nomenclature

Solid	Extraction with toluene	Calcination temperature (ºC)
PS@Si	-	-
@SiexT200	YES	200
@SiT200	-	200
@SiexT300	YES	300
@SiT300	-	300
@SiexT400	YES	400
@SiT400	-	400
@SiexT500	YES	500
@SiT500	-	500

2.4. Characterization

The morphological study of prepared spheres was performed by scanning electron microscopy (SEM), using Philips model 505 equipment. For this determination, the samples were dispersed in ethanol, and an aliquot was dried on a glass sample holder, and subsequently were covered with gold before the analysis.

Thermal analysis of the synthesized materials was carried out by thermogravimetric analysis (TGA) with Shimadzu DT 50 equipment. Determinations were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min. A temperature range between 20 and 650 ºC was studied.

The textural properties of solids were determined from the adsorption-desorption isotherms at the temperature of liquid N_2. The isotherms were obtained using Micromeritics ASAP 2020 equipment. The samples were previously degassed at 100 ºC for 2 h.

The FT-IR spectra of the samples were determined using Bruker IFS 66 equipment and pellets of the sample in KBr, in a wavelength range of 400 to 4000 cm^{-1}.

The solids were studied by transmission electron microscopy (TEM), in a JEOL 100 CXII microscope, working at 100 kV and at a magnification of 80000x. The samples were crushed in an agate mortar, ultrasonically dispersed in isobutanol, and deposited on a carbon-coated copper grid.

3. Results and discussion

Figure 1 presents the SEM micrographs of polystyrene microspheres obtained with two different polymerization initiators. An homogeneous size was observed, with a narrow size distribution, being the average diameter 2.5 μm when ACVA was used as polymerization initiator; when KPS was used spheres with a diameter of 1 μm were obtained and a less homogeneous size distribution. It was observed, for both initiators, that the addition of PVP allows to obtain spheres in suspension without them be grouped in clusters. Both the initiator and the surfactant agent play an important role to obtain stable spheres with a spherical shape.

The difference in the size of the PS particles obtained with the different initiators has been studied in detail by Nomura et al. (2005) who attributed this size difference to different diffusion rates of the initiators. The KPS, soluble in aqueous phase, diffuses at a fast rate toward the monomer drop where polymerization takes place, resulting in particles of smaller diameter. In contrast, the diffusion rate is lower for the organic initiator (ACVA), slowing down the polymerization process and, therefore, particles with larger size are obtained (Nomura et al., 2005). Similar results were obtained by Capek et al. (2001), who considered that the diffusion rate of the initiator molecules is the controlling step of the polymerization rate.

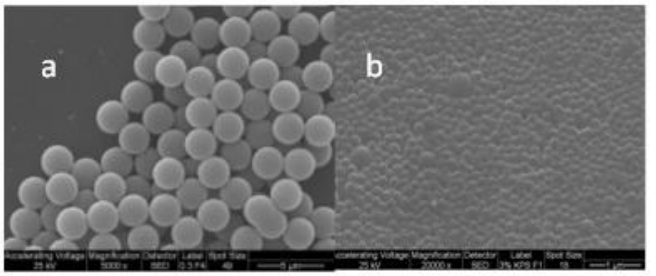

Figure 1. SEM micrographs of polystyrene spheres synthesized using as initiator ACVA (a) or KPS (b).

At first, the coating with silica was carried out using the synthesis conditions that has been reported in the literature (Deng et al, 2006) 7 ml of ammonium hydroxide were used and the coating obtained by deposition of silica was very rough and relatively fragile (Figure 2); a large number of fragmented spheres were observed after extraction treatment with toluene to remove the PS core and subsequent calcination. To overcome this problem, 1 ml of NH_4OH (28% (w/w)) was used as a catalyst for the sol-gel reaction, in an ethanol medium.

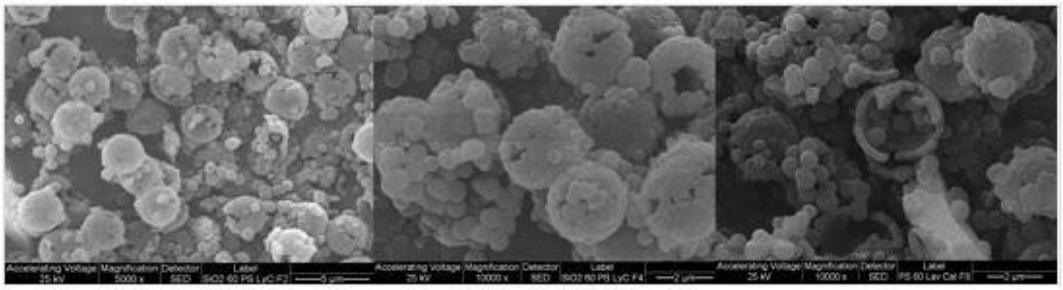

Figure 2. SEM micrographs of hollow silica spheres synthesized using 7 ml of NH_4OH (28% w/w) after 24 h of coating and subsequent removal of the template with toluene and then calcination at 300 ºC.

The NH_4OH quantity used is an important factor in the final characteristics of the material, an adequate amount of catalyst allows obtaining a uniform and resistant coating formed by nanoparticles of silica. This is shown in Figure 3 and Figure 4 obtained by SEM and TEM respectively, where it can be observed coated spheres obtained using 1 ml of NH_4OH (28 %w/w) as a catalyst for the hydrolysis reaction and a time between 14 and 20 h (Figure 3). It was also observed the absence of loose silica or silica forming amorphous aggregates and a coating formed by nanoparticles of silica. The size of SiO_2 nanoparticles on the surface of the PS particles estimated by TEM is approximately between 20 and 50 nm.

The addition of an appropriate amount of catalyst allows controlling the hydrolysis rate of the precursor, giving rise to the possibility that the generated species condense on or in the vicinity of the PS spheres surface and subsequently forming the coating.

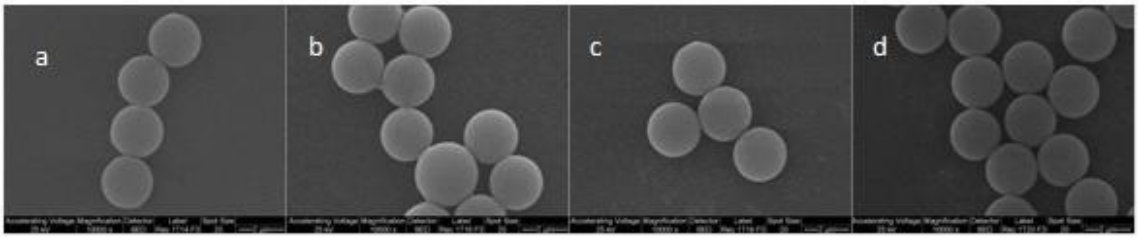

Figure 3. SEM micrographs of polystyrene spheres coated with silica using 1 ml of NH_4OH (28% (w/w)) as a catalyst in the sol-gel reaction after 14 h (a), 16 h (b), 18 h (c) and 20 h (d) of coating, respectively.

The time of coating plays an important role in the process of obtaining the silica shell. It was possible to establish that the thickness of the silica layer obtained at a time higher than 14 h is sufficient enough to maximize the proportion of spheres that will resist the treatment applied for the removal of the PS template without breaking.

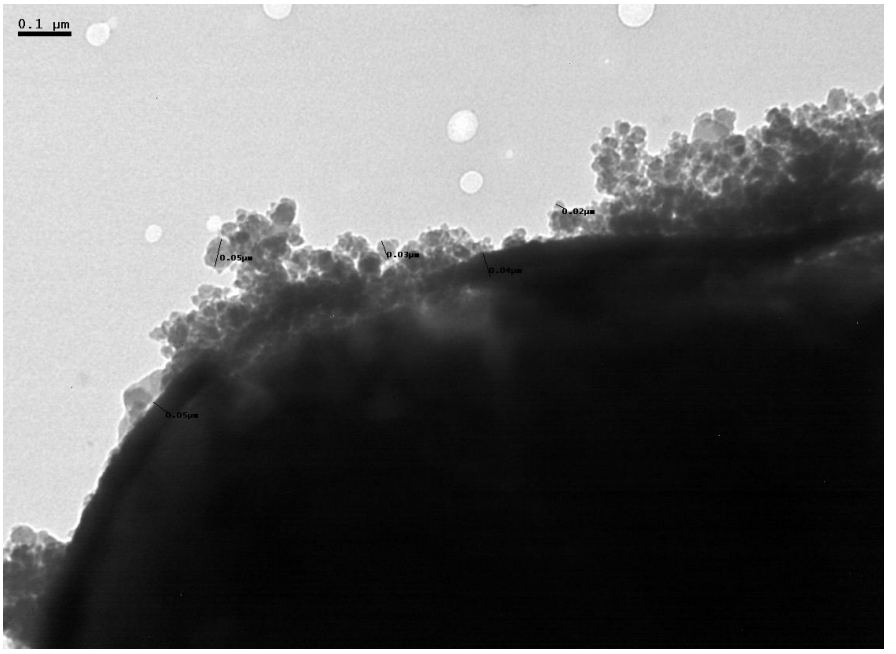

Figure 4. TEM micrographs of polystyrene spheres coated with silica using 1 ml of NH_4OH (28% (w/w)) as a catalyst in the sol-gel reaction.

Figure 5 shows the images of the hollow silica spheres obtained after treatment with toluene and subsequent calcination at 200, 300, 400 and 500 °C. It can be seen the spherical morphology and a smooth surface when the spheres were treated at lower temperatures. As the temperature increases, a large proportion of the material was cracked and broken silica shells can be observed. These results indicate that this methodology to remove the polymer affects the coating of the hollow sphere in an undesired manner.

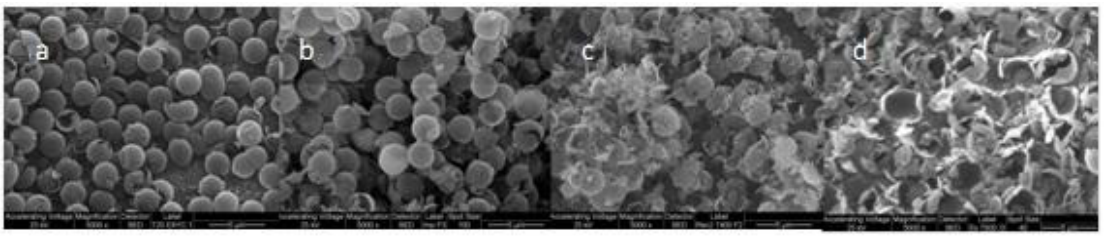

Figure 5. SEM micrographs of hollow silica spheres obtained by extraction with toluene and subsequent calcination at (a) 200 ºC, (b) 300 ºC, (c) 400 °C and (d) 500 ºC.

For the silica-coated PS spheres that were not previously extracted with toluene, it was observed that the coating of silica remains mainly intact even after calcination at 500 ºC (Figure 6). Small holes on the surface indicating the elimination of the polystyrene spheres in order to obtain hollow spheres can also be seen.

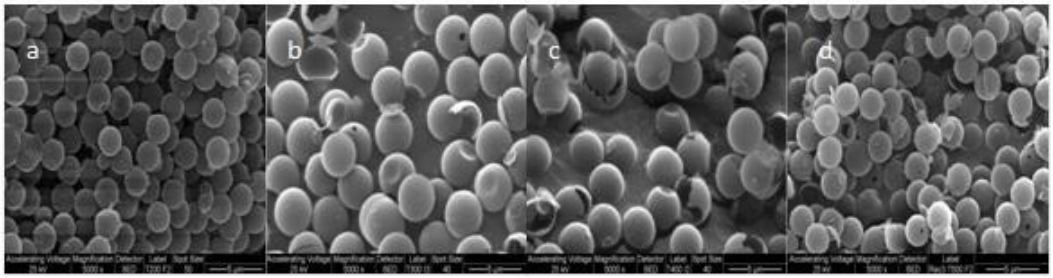

Figure 6. SEM micrographs of hollow silica spheres obtained by only calcination at (a) 200 ºC, (b) 300 ºC, (c) 400 °C and (d) 500 ºC.

Regular and uniform layer consisting of nanoparticles of silica were observed by transmission electronic microscopy measurements (Figure 7) after calcination at different temperatures.

The layer thickness determined from TEM was approximately 100 nm and most of the hollow spheres maintained the spherical shape of the template after calcination at high temperature in agreement with the SEM data.

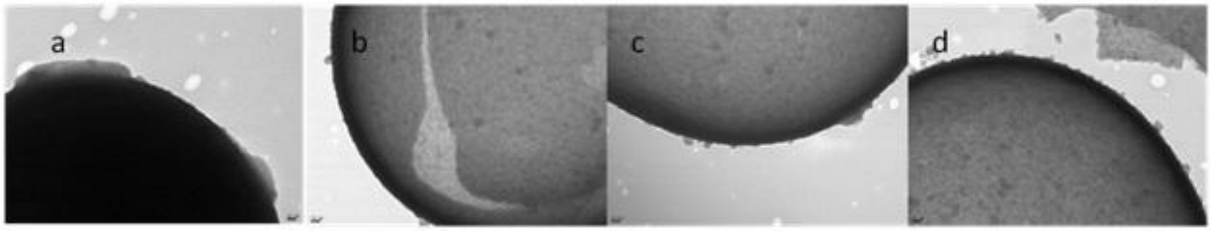

Figure 7. TEM micrographs of hollow silica spheres after calcination at (a) 200 ºC, (b) 300 ºC, (c) 400 °C and (d) 500 ºC.

The FT-IR spectra of the untreated sample (PS@Si), and the @SiexT200, @SiexT300, @SiexT400 and @SiexT500 samples were presented in Figure 8A. In all the samples, there is a band between 3200 and 3700 cm^{-1} corresponding to the asymmetric stretching of the OH group, accompanied by another band at 1600 cm^{-1} assigned to the deformation H-O-H, both indicate free or absorbed water (Venkastewara Rao et al., 1999). For the sample without treatment (PS@Si) some peaks appear between 2850 and 3025 cm^{-1} and a band characteristic of C-H, C-C and C-aromatic groups between 1500 and 1600 cm^{-1} is present, which can be assigned to the polystyrene. For the samples where a removal treatment by extraction was applied and then were calcined, these bands appear in smaller intensity as the temperature of calcination increases. The intense band at 1100 cm^{-1} that appears in all the spectra corresponds to the vibration of the asymmetric stretching of the -OR group; also symmetric stretching of the same group corresponds to the band at 800 cm^{-1} (Vasconcelos et al., 2002).

Figure 8B shows the spectra of the samples only heat treated (@SiT200, @SiT300, @SiT400 and @SiT500). Bands assigned to the polystyrene template appears in the solids treated at 200, 300 and 400 °C. However, for the solid obtained heat treating at 500 ºC these bands of polystyrene disappear.

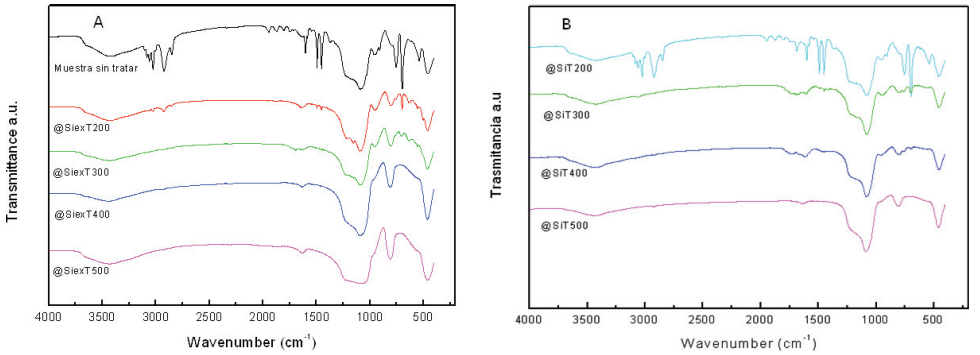

Figure 8. A) FT-IR spectra of the covered spheres :without treatment, and those extracted with toluene and then calcined at 200 ºC, 300 °C, 400 ºC and 500 ºC; B) FT-IR spectra of the spheres calcined at 200 ºC, 300 ºC,400 ºC, and 500 °C.

In Figure 9a, the TGA diagrams of the hollow silica spheres after treated with toluene and subsequently calcined at different temperatures, for the removal of the PS template, were presented. It is observed that both treatments remove in a large proportion the latex spheres, as also was observed in the FT-IR spectra of these materials. When the treatment applied is only calcination at 200 °C, the template elimination is not effective, as can be seen in the TGA diagram in Figure 9b. For the rest of the solids calcined at 300 ºC, 400 ºC and 500 ºC, the removal of the PS spheres did not presented differences with those that were previously treated with toluene, being the elimination of the template equally efficient for these materials.

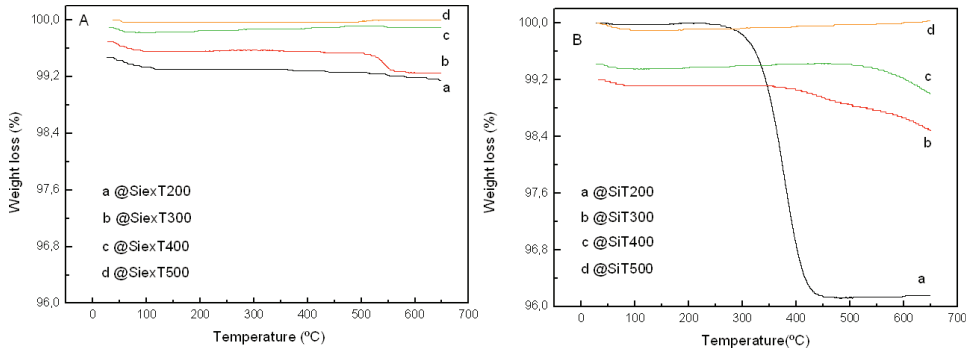

Figure 9. (a) TGA diagrams of samples extracted with toluene and then calcined at 200, 300, 400 and 500 ºC. (b) TGA diagrams of samples calcined at 200, 300, 400 and 500 °C.

The N_2 adsorption-desorption isotherms can be classified as type IV according to the classification of IUPAC. The specific surface area (S_{BET}) together with the average pore diameter (Dp) obtained from the pore size distribution using the Brunauer-Emmet-Teller model are presented in Table 2. The total pore volume (Vp) estimated for a value of $p/p_0 = 0.98$, the specific surface area assigned to the presence of micropores (S_{micro}) and the corresponding pore volume (V_{micro}) estimated by the t-plot method are also listed in Table 2.

Table 2. Textural properties of solids (core removed with toluene and calcined)

Solid	S_{BET} (m^2/g)	S_{micro} (m^2/g)	Vp (cm^3/g)	V_{micro} (cm^3/g)	Dp (nm)
@SiexT200	58	2	0.14	0	9.9
@SiexT300	142	24	0.50	0.01	14.0
@SiexT400	195	65	0.41	0.03	8.3
@SiexT500	190	58	0.40	0.03	8.1

For all the synthesized solids, values of Dp higher than 2 nm were obtained, corresponding mainly to mesoporous solids, being the Vp significantly higher than the micropore volume.

For the prepared materials, as the calcination temperature increases, the amount of PS present in the core decreases, for this reason the Si/PS ratio increases, thus increasing the specific surface area corresponding to the portion of silica in the material.

The hollow silica spheres obtained by calcination at 200, 300, 400 and 500 °C without the pre-treatment with toluene gave S_{BET} values lower than those obtained for the samples extracted with toluene and then calcined. This may be assigned to a partial blockage of the silica pores by PS residues.

4. Conclusions

The PS spheres were coated with a nanoparticle silica layer, with a smooth and uniform morphology as shown in the scanning electron microscopy (SEM) and TEM micrographs. These characteristics were achieved using TEOS as silica precursor, with an adequate amount of NH_4OH (28% w/w) as a catalyst in the sol-gel reaction, and carefully controlling the condensation temperature. To obtain hollow silica spheres two procedures were carried out in parallel; one was carried out by successive washings with toluene and subsequent calcination at 200 ºC, 300 °C, 400 ºC and 500 °C; the other process consisted in only calcination at the same temperatures; both with the purpose of removing the polystyrene core from the prepared materials. For the materials that were previously treated with toluene, it was determined through the FT-IR spectra and the TGA diagrams that the amount eliminated from the core was higher than for those where only calcination was applied, being 500 ºC the calcination temperature that lead to fewer differences between the two procedures. For all the materials an increase in the specific surface area was obtained when the calcination temperature was increased. Through the micrographs obtained by SEM, it is demonstrated that the pretreatment of extraction with toluene of the coated spheres affects in an undesired manner to the hollow spherical structure of silica, yielding even totally fragmented materials. In turn, an almost intact silica shell was observed when only calcination is applied to obtain the hollow spheres.

Acknowledgements

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